

Enhanced phase segregation induced by dipolar interactions in polymer blends

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We present a generalized theory for studying phase separation in blends of polymers containing dipoles on their backbone. The theory is used to construct co-existence curves and to study the effects of dipolar interactions on interfacial tension for a planar interface between the coexisting phases. We show that a mismatch in monomeric dipole moments, or equivalently a mismatch in the dielectric constant of the pure components, leads to destabilization of the homogeneous phase. Corrections to the Flory-Huggins phase diagram are predicted using the theory. Furthermore, we show that the interfacial tension increases with an increase in the mismatch of the dipole moments of the components. Density profiles and interfacial tensions are constructed for diffuse and sharp polymer-polymer interfaces by extending the formalisms of Cahn-Hilliard and Helfand-Tagami-Sapse, respectively.

I. INTRODUCTION

“Like dissolves like” is one of the empirical rules[1] to determine the solubility of solutes in a solvent medium. Similarly, “polar likes polar” is the empirical rule[1] for determining the compatibility among different molecules. In this paper, we derive a theory of this rule in the

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context of polymers and provide a quantitative description of the role played by the polar nature of monomers in determining the commingling of polymers[1–3]. The predictions of the theory are also relevant to the growing usage of dipolar polymers such as peptide-polymer conjugates[4], polypeptoids[5], and polyzwitterions[6].

When the polymer components do not bear any charges or dipoles, the phase behavior is predicted by the classical Flory-Huggins theory [7, 8] by lumping all pair-wise short-ranged interactions into a set of ‘chi’ parameters. This theory has been very successful in capturing various qualitative aspects of phase behavior of uncharged polymers, despite its well-known limitations. Although some improvements can be made by addressing composition fluctuations[9, 10] and monomer architecture[11–13], the presence of long-ranged forces due to charges and dipoles on the chain backbone makes the extension of the Flory-Huggins theory nontrivial. For polymeric systems with ionizable monomers, theories based on field-theoretic treatments[14–20] have borne out to be successful in treating the phase behavior[21–24]. When the repeat groups of the polymer chains carry permanent dipoles, theoretical formulation becomes technically difficult primarily due to the anisotropy of the intersegment orientational interactions and due to its long-range nature. So far, only single chain of dipoles has been addressed[25–28]. It was shown[25] that the dipolar interactions can be treated as freely rotating at higher temperatures, but at lower temperatures chain orientations freeze into a multitude of frustrated conformations.

In this paper, we consider only the high-temperature regime of rotating dipoles without being subjected to frustrated states and address the commingling of two polymer components bearing different dipole moments. We consider the inter-segment interaction to consist of two parts. The first part is the usual contribution from the excluded-volume effect (van der Waals interaction) responsible for the Flory-Huggins ‘chi’ parameter, and the second part is due to point dipoles [1, 29, 30]. The induced dipole moment arising from the polarizability of the molecules necessitating a self-consistent computation is ignored. In addition to calculating the phase diagram, we have followed the formalisms of Cahn-Hilliard [31] and Helfand-Tagami-Sapse [32–35] and calculated the interfacial tension between two coexisting phases and the accompanying density profiles. We show that consideration of dipolar interactions naturally leads to the introduction of a local electric field dependent dielectric function[2, 3, 29, 30, 36–39] in the theory along with its dependence on the temperature and local number density of dipoles. Concentration dependence of the dielectric function

is shown to have significant effects on the phase segregation and interfacial properties. In particular, we have shown that an increase in mismatch between the dipole moments, which is equivalent to an increase in dielectric mismatch between polymer pairs, leads to an enhanced phase segregation as well as sharper interfaces. As a result of sharper interfaces, interfacial tension for an interface between the coexisting phases increases with an increase in the dielectric mismatch. Also, these predictions are compared with theoretical treatment for freely rotating dipoles[1, 25, 27, 28], which is valid only at very high temperatures.

The rest of the paper is organized as follows: the formalism is presented in section II, followed by the results in section III and conclusions in section IV.

II. THEORY

We consider a polymer blend containing n_A, n_B flexible chains of type A and B , respectively. In this work, we consider monodisperse polymer chains so that each chain has N_j Kuhn segments of length b_j for $j = A, B$. Representing each chain as a continuous curve of length $N_j b_j$, an arc length variable $s_{j,\alpha}$ is used to represent any segment along the backbone of α^{th} chain of kind j so that $s_{j,\alpha} \in [0, N_j]$. Furthermore, each segment on a chain is assigned an electric dipole of length p_j so that the dipole moment is of magnitude ep_j (e being the electronic charge), where $j = A, B$. Although we have not taken into account the variations in the magnitude of these electric dipole moments, but we allow the dipoles to be aligned depending on the local electric field. The physical origin of these electric dipoles is the polar nature of the monomers used to synthesize the polymers such as poly(ethylene oxide) and bipolymers like polypeptoids[5]. For example, a difference in electronegativities of oxygen and carbon leads to a dipole moment of 1.9 Debye for ethylene oxide monomer[1]. An important point regarding the origin of electric dipoles is worth mentioning here. In addition to the inherent dipole moments of the molecules, finite polarizability of molecules leads to induced electric moments[2, 3] in the presence of other molecules. This induction effect, in turn, enhances[2, 3] the net electric dipole moments. In this work, as a first step we study the effects of “permanent dipole moments” only and neglect the effects of “induced dipole moments” which is more relevant for highly polarizable or polymers with no permanent moments.

The thermodynamic properties of a two-component dipolar polymeric system modeled

as above are derived from the partition function defined through an effective coarse-grained Hamiltonian[40, 41] and by following the now-standard field theoretic technique[42–47]. The partition function Z is written as a functional path integral over various allowed conformations of all chains and orientations of all segments as

$$Z = \frac{1}{n_A!n_B!} \int \prod_{j=A,B} \prod_{\alpha=1}^{n_j} D[\mathbf{R}_{j,\alpha}] \int \prod_{\alpha=1}^{n_j} \prod_{s_{j,\alpha}=0}^{N_j} d\mathbf{u}_{j,\alpha}(s_{j,\alpha}) \exp [-H_0 \{\mathbf{R}_{j,\alpha}\} - H_w \{\mathbf{R}_{j,\alpha}, \mathbf{R}_{j',\alpha'}\} - H_{dd} \{\mathbf{R}_{j,\alpha}, \mathbf{u}_{j,\alpha}, \mathbf{R}_{j',\alpha'}, \mathbf{u}_{j',\alpha'}\}] \prod_{\mathbf{r}} \delta [\hat{\rho}_A(\mathbf{r}) + \hat{\rho}_B(\mathbf{r}) - \rho_0]. \quad (1)$$

Here the Hamiltonian is written by taking into account the contributions from the chain connectivity (given by H_0 in Eq. (2) below), the short ranged repulsive hard-core and attractive dispersive interactions other than the permanent dipole-dipole (represented by H_w in Eq. (3)) and the long range electrostatic interactions between the dipolar species (written as H_{dd} , which corresponds to the segment-segment interactions). Explicitly, the contribution from the chain connectivity is modeled as the Wiener measure[41, 47, 48]

$$H_0 \{\mathbf{R}_{j,\alpha}\} = \sum_{j=A,B} \frac{3}{2b_j^2} \sum_{\alpha=1}^{n_j} \int_0^{N_j} ds_{j,\alpha} \left(\frac{\partial \mathbf{R}_{j,\alpha}(s_{j,\alpha})}{\partial s_{j,\alpha}} \right)^2. \quad (2)$$

$H_w \{\mathbf{R}_{j,\alpha}, \mathbf{R}_{j',\alpha'}\}$ takes into account the energetic contributions arising from short-range dispersion interactions between segments of chains indexed as α and α' located at $\mathbf{R}_{j,\alpha}$ and $\mathbf{R}_{j',\alpha'}$, respectively. Following the Edwards formulation for a flexible chain[41], we model these interactions by delta functional/point interactions as[40, 43]

$$H_w \{\mathbf{R}_{j,\alpha}, \mathbf{R}_{j',\alpha'}\} = \frac{1}{2} \int d\mathbf{r} [w_{AA} \hat{\rho}_A^2(\mathbf{r}) + w_{BB} \hat{\rho}_B^2(\mathbf{r}) + 2w_{AB} \hat{\rho}_A(\mathbf{r}) \hat{\rho}_B(\mathbf{r})] \quad (3)$$

Here, w_{AA} , w_{BB} and w_{AB} are the well-known excluded volume parameters describing the strengths of interactions between $A - A$, $B - B$ and $A - B$ monomeric pairs, respectively. These parameters characterize strength of short-ranged interactions, whose range is parameterized by using delta function interaction potentials. Also, $\hat{\rho}_j(\mathbf{r})$ represents microscopic number density of the monomers of type j at a certain location \mathbf{r} defined as

$$\hat{\rho}_j(\mathbf{r}) = \sum_{\alpha=1}^{n_j} \int_0^{N_j} ds_{j,\alpha} \delta [\mathbf{r} - \mathbf{R}_{j,\alpha}(s_{j,\alpha})] \quad \text{for } j = A, B \quad (4)$$

Electrostatic contributions to the Hamiltonian arising from the segment-segment (or dipole-dipole) interactions can be written as[30]

$$H_{dd} = \frac{l_{Bo}}{2} \int d\mathbf{r} \int d\mathbf{r}' \int d\mathbf{u} \int d\mathbf{u}' \hat{P}(\mathbf{r}, \mathbf{u}) V_{dd}(\mathbf{r}, \mathbf{u}, \mathbf{r}', \mathbf{u}') \hat{P}(\mathbf{r}', \mathbf{u}') \quad (5)$$

where $l_{Bo} = e^2/\epsilon_o k_B T$ is the Bjerrum length in vacuum, ϵ_o is the permittivity of vacuum and $k_B T$ is the Boltzmann constant times the absolute temperature. The dipolar potential V_{dd} is given by[1, 25, 28]

$$V_{dd}(\mathbf{r}, \mathbf{u}, \mathbf{r}', \mathbf{u}') = \frac{\mathbf{u} \cdot \mathbf{u}'}{|\mathbf{r} - \mathbf{r}'|^3} - 3 \frac{\{\mathbf{u} \cdot (\mathbf{r} - \mathbf{r}')\} \{\mathbf{u}' \cdot (\mathbf{r} - \mathbf{r}')\}}{|\mathbf{r} - \mathbf{r}'|^5} \quad (6)$$

and $\hat{P}(\mathbf{r}, \mathbf{u}) = p_A \bar{\rho}_A(\mathbf{r}, \mathbf{u}) + p_B \bar{\rho}_B(\mathbf{r}, \mathbf{u})$ is the local dipole density at \mathbf{r} in the direction of the unit vector specified by unit vector \mathbf{u} centered at the location of \mathbf{r} . Here, we have defined a microscopic number density of dipoles of type A and B by $\bar{\rho}_A(\mathbf{r}, \mathbf{u})$ and $\bar{\rho}_B(\mathbf{r}, \mathbf{u})$, respectively. Physically, these functions describe the number of dipoles with their centers at a certain location \mathbf{r} with their axes oriented along the unit vector \mathbf{u} . Formally, these are defined as

$$\bar{\rho}_j(\mathbf{r}, \mathbf{u}) = \sum_{\alpha=1}^{n_j} \int_0^{N_j} ds_{j,\alpha} \delta[\mathbf{r} - \mathbf{R}_{j,\alpha}(s_{j,\alpha})] \delta[\mathbf{u} - \mathbf{u}_{j,\alpha}(s_{j,\alpha})] \quad \text{for } j = A, B \quad (7)$$

As with the Edwards Hamiltonian for short range inter-segment interactions leading to divergences at short length scales (ultraviolet divergence), the dipolar potential (Eq. 6) also diverges at $|\mathbf{r} - \mathbf{r}'| \rightarrow 0$. We have regularized these divergences by introducing a short range cut-off length of the order of the Kuhn segment length.

Furthermore, we have imposed the incompressibility constraint of the system with the use of the delta function in Eq. 1. The factorials in Eq. 1 represent the indistinguishability of the chains for each component.

A. Freely rotating dipoles : spinodal, structure factor and interfacial tension

At high temperatures or for small dipole moments (so that $l_{Bo} p_j \ll 1$ for $j = A, B$), dipoles can rotate freely[1]. The condition of free rotation by segmental dipoles is representative of a disordered melt at high temperatures. For this particular case, the structure factor and the spinodal curves corresponding to the limits of thermodynamic stability can be computed in a relatively straightforward manner as described below. For freely rotating

dipoles ($l_{Bo}p_j \ll 1$), we can use a series expansion in powers of dipole moments and integrate out the orientational degrees of freedom. Truncating the series after fourth power of the dipole moments and exponentiating the series[1, 28], the partition function for freely rotating dipoles $Z = \hat{Z}$ (cf. Eq. 1) can be written as

$$\hat{Z} = \frac{(4\pi)^{\sum_{j=A,B} n_j N_j}}{n_A! n_B!} \int \prod_{j=A,B} \prod_{\alpha=1}^{n_j} D[\mathbf{R}_{j,\alpha}] \exp[-H_0 \{\mathbf{R}_{j,\alpha}\} - H_w \{\mathbf{R}_{j,\alpha}, \mathbf{R}_{j',\alpha'}\} - \hat{H}_{dd} \{\mathbf{R}_{j,\alpha}, \mathbf{R}_{j',\alpha'}\}] \prod_{\mathbf{r}} \delta[\hat{\rho}_A(\mathbf{r}) + \hat{\rho}_B(\mathbf{r}) - \rho_0] \quad (8)$$

where the angularly averaged dipolar interaction term, \hat{H}_{dd} , is given by

$$\hat{H}_{dd} = -\frac{l_{Bo}^2}{12} \int d\mathbf{r} \int d\mathbf{r}' \frac{[p_A^2 \hat{\rho}_A(\mathbf{r}) + p_B^2 \hat{\rho}_B(\mathbf{r})][p_A^2 \hat{\rho}_A(\mathbf{r}') + p_B^2 \hat{\rho}_B(\mathbf{r}')] }{|\mathbf{r} - \mathbf{r}'|^6} \quad (9)$$

The dipole interaction in the limit of free rotation becomes essentially short ranged[1, 27]. Within the random phase approximation[42–44, 46, 49, 50], the free energy up to the fourth degree terms in the order parameter $C(\mathbf{r}) = \hat{\rho}_A(\mathbf{r})/\rho_0 - \phi_A = 1 - \phi_A - \hat{\rho}_B(\mathbf{r})/\rho_0$ ($\phi_A = n_A N_A / \rho_0 V$ being the average volume fraction of A monomers, where ρ_0 being the average density and V is the total volume of the homogeneous system) is given by

$$\exp \left[-\frac{(\hat{F} - \hat{F}_H)}{k_B T} \right] = \int \prod_{k \neq 0} D[C_k] \exp \left[-\frac{\delta F\{C_k\}}{k_B T} \right] \quad (10)$$

where

$$\begin{aligned} \frac{\delta F\{C_k\}}{k_B T} &= \frac{\rho_0}{2} \sum_{k \neq 0} S^{-1}(k) C_k C_{-k} + \frac{\rho_0}{6} \sum_{k_1, k_2} \Gamma_3(k_1, k_2, -k_1 - k_2) C_{k_1} C_{k_2} C_{-k_1 - k_2} \\ &+ \frac{\rho_0}{12} \sum_{k_1, k_2, k_3} \Gamma_4(k_1, k_2, k_3, -k_1 - k_2 - k_3) C_{k_1} C_{k_2} C_{k_3} C_{-k_1 - k_2 - k_3} \end{aligned} \quad (11)$$

In these expressions, k, k_j are the wavevectors and C_k is the Fourier component of $C(\mathbf{r})$. \hat{F}_H is the free energy of the homogeneous phase (corresponding to $k = 0$), given by

$$\begin{aligned} \frac{\hat{F}_H}{\rho_0 V k_B T} &= \frac{\rho_0}{2} [w_{AA} \phi_A + w_{BB} (1 - \phi_A)] + \frac{\phi_A}{N_A} \left[\ln \left(\frac{\phi_A}{N_A} \right) - 1 \right] + \frac{(1 - \phi_A)}{N_B} \left[\ln \left(\frac{1 - \phi_A}{N_B} \right) - 1 \right] \\ &+ \chi_{AB} \phi_A (1 - \phi_A) - \frac{\pi \rho_0 l_{Bo}^2}{9 \lambda^3} [p_A^2 \phi_A + p_B^2 (1 - \phi_A)]^2 - \ln 4\pi \end{aligned} \quad (12)$$

where λ is a cut-off length below which $1/r^6$ dipolar potential is no longer valid. Also, we have defined

$$\chi_{AB} b^3 = w_{AB} - \frac{w_{AA} + w_{BB}}{2} \quad (13)$$

and used $\rho_0 b^3 = 1$ in writing Eq. 12. Spinodal curve can be computed using Eq. 12 and is given by

$$\frac{\partial^2}{\partial \phi_A^2} \left[\frac{\hat{F}_H}{\rho_0 V k_B T} \right] = \frac{1}{\phi_A N_A} + \frac{1}{(1 - \phi_A) N_B} - 2\chi_{AB} - \frac{2\pi \rho_0 l_{Bo}^2}{9\lambda^3} [p_A^2 - p_B^2]^2 = 0 \quad (14)$$

It is clear from this expression that dipolar interactions renormalizes “chi” parameter and we can write an “effective” parameter as

$$\chi_{AB,eff} = \chi_{AB} + \frac{p^4}{16\pi \rho_0 \lambda^3} \quad \text{where} \quad p^2 = \frac{4\pi}{3} l_{Bo} \rho_0 (p_A^2 - p_B^2) \quad (15)$$

, which is in accord with the well-known law, “polar likes polar”. Also, note that the Edwards’ approach for using a delta function potential in order to model short range interactions along with the local incompressibility constraint naturally leads to appearance of the dimensionless Flory’s chi parameter χ_{AB} in the theory, defined in terms of excluded volume parameters w_{AA}, w_{BB} and w_{AB} by Eq. 13. The physical origin of the excluded volume parameters[8] is the repulsive hard-core and attractive dispersive interactions and in general, $w_{ij} = w_{ij}^0 - \omega \alpha_i \alpha_j$ so that $\omega > 0$ (the dispersive interactions being attractive), α_i is the electronic polarizability of molecule i and w_{ij}^0 is the volume excluded due to hard-cores. Using the definition of χ_{AB} in terms of excluded volume parameters, it has been postulated[8] that $\chi_{AB} b^3 = \chi_{AB}^0 b^3 + \omega(\alpha_A - \alpha_B)^2/2 > 0$ where $\chi_{AB}^0 b^3 = w_{AB}^0 - \frac{w_{AA}^0 + w_{BB}^0}{2}$. Additional contribution in $\chi_{AB,eff} b^3$ arising from dipolar interactions is in qualitative agreement with such a description of the “chi” parameter in terms of electronic polarizabilities if we invoke the relation for total polarizability of a molecule of type j as $\alpha_j = \alpha_o + p_j^2/3k_B T$ (known as the Debye-Langevin[1] equation, which is strictly valid at high temperatures), where α_o is the electronic polarizability and the rest is the orientational polarizability.

For uncharged polymers, the spinodal ‘chi’ parameter χ_{s0} follows from Eq. 14 as

$$2\chi_{s0} = \frac{1}{\phi_A N_A} + \frac{1}{(1 - \phi_A) N_B}. \quad (16)$$

Writing this as being proportional to the inverse of temperature T_{s0} , and noting that the Bjerrum length l_{Bo} is inversely proportional to T , the spinodal temperature T_s for the presence of dipole moment mismatch follows from Eq. 14 as

$$\frac{T_s}{T_{s0}} = \frac{1}{2} \left[1 + \left\{ 1 + \frac{4\pi \rho_0}{9\chi_{s0} \lambda^3} \left(\frac{e^2}{\epsilon_0 k_B T_{s0}} \right)^2 (p_A^2 - p_B^2)^2 \right\}^{1/2} \right]. \quad (17)$$

Therefore, the spinodal temperature is increased by the mismatch in the dipole moments of the components. This result based on freely rotating dipolar segments turns out to be a general result as shown below.

Furthermore, effects of dipolar interactions on the structure factor and correlation length can be studied by analyzing the second order term in Eq. 11, which is the inverse of the structure factor, $S^{-1}(k)$, given by

$$S^{-1}(k) = S_{bare}^{-1}(k) + S_{dd}^{-1}(k) \quad (18)$$

$$\text{so that } S_{bare}^{-1}(k) = \frac{1}{\phi_A N_A g(x_A)} + \frac{1}{(1 - \phi_A) N_B g(x_B)} - 2\chi_{AB} \quad (19)$$

$$\text{and } S_{dd}^{-1}(k) = -\frac{p^4}{8\pi\rho_0} \left[\frac{1}{\lambda^3} - \frac{k^2}{2\lambda} + \frac{\pi k^3}{16} \right] \quad (20)$$

In Eq. 18, $S_{bare}^{-1}(k)$ is the contribution due to Gaussian chains interacting via short range excluded volume interactions and $S_{dd}^{-1}(k)$ is the additional effect due to the dipolar interactions present in the system. In writing Eq. 20, we have used mathematical expression for Fourier Transform (FT) of $1/r^6$, given by $\text{FT}(1/r^6) = 4\pi \int_0^\infty dr \frac{\sin kr}{kr^5} = \frac{4\pi}{3} \left[\frac{1}{\lambda^3} - \frac{k^2}{2\lambda} + \frac{\pi k^3}{16} \right]$ so that $\lambda \rightarrow 0$ is the cutoff length included to regularize divergent integrals. Also, $g(x_j)$ is the Debye function[41, 47] given by

$$g(x_j) = \frac{2(e^{-x_j} - 1 + x_j)}{x_j^2}, \quad x_j = \frac{k^2 N_j b_j^2}{6} = k^2 R_{g,j}^2 \quad (21)$$

The correlation length[8] ξ in dipolar polymer blends can be extracted from Eq. 18 by using an expansion[8, 41] of the Debye function at small wavevectors k ($g(x_j) \rightarrow 1 - x_j/3$ for $x_j < 1$). The approximation for the Debye function lets us write

$$S^{-1}(k) = \frac{1}{\phi_A N_A} + \frac{1}{(1 - \phi_A) N_B} - 2\chi_{AB,eff} + \frac{k^2}{18} \left[\frac{b_A^2}{\phi_A} + \frac{b_B^2}{1 - \phi_A} + \frac{9p^4}{8\pi\rho_0\lambda} \right] \quad (22)$$

where we have kept terms up to k^2 . Writing $S(k) = S(0)/(1 + k^2\xi^2)$, ξ is given by

$$\xi = \frac{1}{\sqrt{18}} \left[\frac{b_A^2}{\phi_A} + \frac{b_B^2}{1 - \phi_A} + \frac{9p^4}{8\pi\rho_0\lambda} \right]^{1/2} \left[\frac{1}{\phi_A N_A} + \frac{1}{(1 - \phi_A) N_B} - 2\chi_{AB,eff} \right]^{-1/2} \quad (23)$$

From Eqs. 15 and 23, it is clear that the correlation length increases with an increase in mismatch between the monomeric dipole moments. Also, using Eqs. 14 and 23, the correlation length ξ diverges at the critical point $T = T_c$ with the exponent of $-1/2$.

Effects of dipolar interactions on the correlation length manifest in the density profiles as well as interfacial tension of the interface between coexisting phases near the critical

point. Using Eqs. 10 and 11, we have studied interfacial tension between co-existing phase near the critical point within the saddle-point approximation. Approximating $S^{-1}(k)$ by Eq. 22, $\Gamma_3(k_1, k_2, k_3)$ and $\Gamma_4(k_1, k_2, k_3, k_4)$ by their value[49, 50] at $|k_j| = 0$, we have constructed density profiles and the interfacial tension. Using such a procedure leads to a volume fraction profile[31, 51] given by

$$\phi_A(z) = \phi_{A,c} + \frac{[\phi_A(\infty) - \phi_A(-\infty)]}{2} \tanh \left[\frac{z}{\sqrt{2}\xi_c} \right] \quad (24)$$

where z is the direction perpendicular to the interface and $\phi_{A,c}$ is the volume fraction of A at the critical point. Furthermore, $\phi_A(\pm\infty) = \phi_{A,c} \pm \sqrt{3|\Gamma_2(0)|/\Gamma_4(0)}$ so that $\Gamma_2(0) = [S^{-1}(0)]_{\phi_A=\phi_{A,c}}$, $\xi_c = [\xi]_{\phi_A=\phi_{A,c}}$ and

$$\Gamma_4(0) = \frac{1}{\phi_{A,c}^3 N_A} + \frac{1}{(1 - \phi_{A,c})^3 N_B} \quad (25)$$

It is to be noted that the volume fraction in the phase at $z \rightarrow \infty$ tends to increase with an increase in the mismatch between the monomeric dipole moments. In other words, an increase in the mismatch tends to promote phase segregation. From Eq. 12, the volume fraction at the critical point is given by

$$\phi_{A,c} = \frac{\sqrt{N_B}}{\sqrt{N_A} + \sqrt{N_B}} \quad (26)$$

and stays the same as in the absence of dipolar interactions. In the next section, we will show that this is a direct consequence of the neglect of orientational effects in the case of freely rotating dipoles and in fact, critical point gets shifted by dipolar interactions.

Nevertheless, using Eq. 24 for the volume fraction profile, interfacial tension near the critical point, σ_c , (per unit area) can be readily computed, given by

$$\frac{\sigma_c}{Ak_B T} = \frac{2\sqrt{2}\Gamma_2(0)^2\xi_c}{\Gamma_4(0)} = \frac{2}{3} \frac{|\Gamma_2(0)|^{3/2}}{\Gamma_4(0)} \left[\frac{b_A^2}{\phi_{A,c}} + \frac{b_B^2}{1 - \phi_{A,c}} + \frac{9p^4}{8\pi\rho_0\lambda} \right]^{1/2} \quad (27)$$

where A is the area of the planar interface.

From Eq. 27, it is clear that the interfacial tension increases with an increase in mismatch between the dipole moments of the two monomers in polymer blends. Also, Eqs. 23 and 24 reveal that interfacial width ($= \sqrt{2}\xi_c$) *increases* with an increase in the mismatch i.e., interfaces become more diffuse with an increase in the mismatch. Note that the approximation of freely rotating dipoles is strictly valid in the high temperature limit close to one phase regime and it is clear that such an approximation will be invalid in the two

phase regime. In order to study inhomogeneous structures such as a sharp interface between coexisting phases, we need to construct a theory capable of taking into account the effects of inhomogeneities on the dipolar interactions. In the following, we present such a general formalism using field theoretical transformations[47] and use it to study coexistence curves as well as the interfacial tension. Predictions of the field theory are contrasted with the predictions presented above for freely rotating dipoles.

B. Field theory

Before introducing fields, we can write the electrostatic terms in a more convenient form by defining a quantity $\hat{P}_{ave}(\mathbf{r}) = \int d\mathbf{u} \hat{P}(\mathbf{r}, \mathbf{u}) \mathbf{u}$, which is a vector. H_{dd} in Eq. 5 can be written in terms of $\hat{P}_{ave}(\mathbf{r})$ as

$$H_{dd} = \frac{l_{Bo}}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{[\nabla_{\mathbf{r}} \cdot \hat{P}_{ave}(\mathbf{r})] [\nabla_{\mathbf{r}'} \cdot \hat{P}_{ave}(\mathbf{r}')]}{|\mathbf{r} - \mathbf{r}'|} \quad (28)$$

Using field theoretical transformations described in Appendix A, we can write the partition function for the blends as

$$Z = \frac{Z_o}{\mu_\psi} \int D[\rho_A] \int D[w_A] \int D[w_B] \int D[\psi] \exp \left[-\frac{H}{k_B T} \right] \quad (29)$$

where $Z_o = \exp(-\frac{F_0}{k_B T})$ is the partition function for the same system in the absence of the interactions, given by

$$\frac{F_0}{k_B T} = \frac{1}{2} [w_{AA} n_A N_A + w_{BB} n_B N_B] \rho_0 + \ln \left[\frac{n_A! n_B!}{(4\pi)^{n_A N_A + n_B N_B} V^{n_A + n_B}} \right] \quad (30)$$

and

$$\begin{aligned} \frac{H}{k_B T} = & \chi_{AB} b^3 \int d\mathbf{r} \rho_A(\mathbf{r}) (\rho_0 - \rho_A(\mathbf{r})) - i \int d\mathbf{r} w_A(\mathbf{r}) \rho_A(\mathbf{r}) - i \int d\mathbf{r} w_B(\mathbf{r}) [\rho_0 - \rho_A(\mathbf{r})] \\ & - \frac{1}{8\pi l_{Bo}} \int d\mathbf{r} \psi(\mathbf{r}) \nabla_{\mathbf{r}}^2 \psi(\mathbf{r}) - \int d\mathbf{r} \rho_A(\mathbf{r}) \ln \left[\frac{\sin(p_A |\nabla_{\mathbf{r}} \psi(\mathbf{r})|)}{p_A |\nabla_{\mathbf{r}} \psi(\mathbf{r})|} \right] \\ & - \int d\mathbf{r} \{ \rho_0 - \rho_A(\mathbf{r}) \} \ln \left[\frac{\sin(p_B |\nabla_{\mathbf{r}} \psi(\mathbf{r})|)}{p_B |\nabla_{\mathbf{r}} \psi(\mathbf{r})|} \right] - \sum_{j=A,B} n_j \ln \bar{Q}_j \{w_j\} \end{aligned} \quad (31)$$

Here, \bar{Q}_j is *normalized* partition functions for a polymer chain of type j described explicitly in Appendix A. In these equations, ψ is the collective field introduced to decouple electrostatic interactions and is the equivalent of electrostatic potential. Also, w_A, w_B are

the fields introduced to decouple short range interactions modeled by Edwards' delta functional approach[41, 47]. Furthermore, ρ_A is collective variable characterizing local density of monomers of type A .

It is clear from the partition function (cf. Eqs. 29 and 31) that the parameters $p_A|\nabla_{\mathbf{r}}\psi(\mathbf{r})|$ and $p_B|\nabla_{\mathbf{r}}\psi(\mathbf{r})|$ are the parameters controlling the magnitude of the effect of electric dipoles on the thermodynamics. An important insight into the effect of electric dipoles on the thermodynamics of the blends is obtained if one considers the weak coupling limit[30] for the electric dipoles (i.e., the limit of weak dipoles or weak local electric fields) so that $p_A|\nabla_{\mathbf{r}}\psi(\mathbf{r})| \rightarrow 0$, $p_B|\nabla_{\mathbf{r}}\psi(\mathbf{r})| \rightarrow 0$ (note that the “weak coupling limit” considered in this work is different from the one used in literature[52, 53] on electrolytes characterized by the coupling constant $z\psi$, z being the charge). In this limit, we can use the approximation $\ln[\sin x/x] \simeq -x^2/6$ in the expression for the partition function. Using the approximations, it can be shown that the electric dipoles renormalize the Bjerrum length of the medium by the relation

$$\frac{1}{l_B(\mathbf{r})} = \frac{1}{l_{Bo}} + \frac{4\pi}{3} [p_A^2\rho_A(\mathbf{r}) + p_B^2(\rho_0 - \rho_A(\mathbf{r}))] \quad (32)$$

where $l_B(\mathbf{r})$ is the renormalized Bjerrum length in the polymer blend. One can also use this relation to define an effective local dielectric function if we use the relation between the Bjerrum length and the dielectric constant as $l_B(\mathbf{r}) = e^2/\epsilon_o\epsilon(\mathbf{r})k_BT$. This allows us to write,

$$\epsilon(\mathbf{r}) = \epsilon_A\phi_A(\mathbf{r}) + \epsilon_B\phi_B(\mathbf{r}), \quad (33)$$

where $\phi_A(\mathbf{r}) = \rho_A(\mathbf{r})/\rho_0$ and $\phi_B(\mathbf{r}) = (\rho_0 - \rho_A(\mathbf{r}))/\rho_0$ are the volume fractions of A and B monomers, respectively. Furthermore, *relative* dielectric “constant” of the pure components (with respect to vacuum) are given by the relations

$$\epsilon_A = 1 + \frac{4\pi l_{Bo}}{3} p_A^2 \rho_0 \quad (34)$$

$$\epsilon_B = 1 + \frac{4\pi l_{Bo}}{3} p_B^2 \rho_0. \quad (35)$$

Note that Eq. 33 for the local dielectric function is valid, in general, for the homogeneous as well as inhomogeneous systems. In the subsequent section, we present the implications of the concentration dependence and inhomogeneous nature of the dielectric function on the thermodynamics of polymer blends. In the weak coupling limit, functional integral over ψ can be computed exactly for one-dimensional variation in densities e.g., in the case of a planar

interface between the co-existing phases. In the following, we present details of method of evaluating the functional integral. After the evaluation, we approximate other functional integrals by the saddle-point approximation to construct a free energy expression. Due to the fact that the functional integral over ψ is computed without invoking the saddle-point approximation, the results presented in this work goes beyond the mean-field description of electrostatics.

C. Electrostatic contribution

We start by rewriting Eq. 29 as

$$Z = Z_o \int D[\rho_A] \int D[w_A] \int D[w_B] \exp \left[-\frac{H_{neu} - H_{elec}}{k_B T} \right] \quad (36)$$

where

$$\begin{aligned} \frac{H_{neu}}{k_B T} = & \chi_{AB} b^3 \int d\mathbf{r} \rho_A(\mathbf{r}) (\rho_0 - \rho_A(\mathbf{r})) - i \int d\mathbf{r} w_A(\mathbf{r}) \rho_A(\mathbf{r}) - i \int d\mathbf{r} w_B(\mathbf{r}) [\rho_0 - \rho_A(\mathbf{r})] \\ & - \sum_{j=A,B} n_j \ln \bar{Q}_j \{w_j\} \end{aligned} \quad (37)$$

and

$$\frac{H_{elec}}{k_B T} = -\ln \left[\frac{\int D[\psi] \exp \left(-\frac{1}{8\pi l_{Bo}} \int d\mathbf{r} \epsilon(\mathbf{r}) |\nabla_{\mathbf{r}} \psi(\mathbf{r})|^2 \right)}{\int D[\psi] \exp \left(-\frac{1}{8\pi l_{Bo}} \int d\mathbf{r} |\nabla_{\mathbf{r}} \psi(\mathbf{r})|^2 \right)} \right] \quad (38)$$

and $\epsilon(\mathbf{r})$ is given by Eq. 33. In the following, we rewrite Eq. 33 as

$$\epsilon(\mathbf{r}) = \epsilon_B + p^2 \rho_A(\mathbf{r}) / \rho_o \quad (39)$$

$$\text{so that } p^2 = \frac{4\pi l_{Bo} \rho_o}{3} (p_A^2 - p_B^2) = \epsilon_A - \epsilon_B \quad (40)$$

where ϵ_A and ϵ_B are the dielectric constants for the pure “A” and “B” phases, respectively. (cf. Eqs. 34 and 35). Also, the parameter p is the same as defined in Eq. 15 while considering freely-rotating dipoles. In general, computation of H_{elec} is a hard problem due to need to compute all eigenvalues of the operator in the exponent. However, for one dimensional variation in the volume fraction (and in turn, the dielectric function), $H_{elec}/k_B T$ can be computed exactly by writing it as

$$\frac{H_{elec}}{k_B T} = -\ln \left[\frac{\int D[\psi] \exp \left(\frac{1}{8\pi l_{Bo}} \int d\mathbf{r} \psi(\mathbf{r}) \nabla_{\mathbf{r}} \cdot \{ \epsilon(\mathbf{r}) \nabla_{\mathbf{r}} \psi(\mathbf{r}) \} \right)}{\int D[\psi] \exp \left(\frac{1}{8\pi l_{Bo}} \int d\mathbf{r} \psi(\mathbf{r}) \nabla_{\mathbf{r}}^2 \psi(\mathbf{r}) \right)} \right] \quad (41)$$

where we have used integration by parts and the fact that $\nabla_{\mathbf{r}}\psi(\mathbf{r}) = 0$ at the boundaries. For one-dimensional variations in dielectric function so that $\epsilon(\mathbf{r}) \equiv \epsilon(z)$, we can use two-dimensional Fourier-Transform for $\psi(\mathbf{r})$ defined by $\psi(\mathbf{r}) = \sum_{\mathbf{q}} \hat{\psi}_{\mathbf{q}}(z) \exp^{i\mathbf{q}\cdot\mathbf{r}_{\parallel}}$, \mathbf{r}_{\parallel} being an in-plane position vector. Using the Fourier-Transform, Eq. 41 becomes

$$\frac{H_{elec}}{k_B T} = - \sum_{\mathbf{q}} \ln \left[\frac{\int D[\hat{\psi}_{\mathbf{q}}(z)] \exp \left(-\frac{1}{2} \int_0^L dz \hat{\psi}_{\mathbf{q}}(z) M_{\mathbf{q}}(z) \hat{\psi}_{-\mathbf{q}}(z) \right)}{\int D[\hat{\psi}_{\mathbf{q}}(z)] \exp \left(-\frac{1}{2} \int_0^L dz \hat{\psi}_{\mathbf{q}}(z) \hat{M}_{\mathbf{q}}(z) \hat{\psi}_{-\mathbf{q}}(z) \right)} \right] \quad (42)$$

where

$$M_{\mathbf{q}}(z) = \frac{\epsilon(z)}{4\pi l_{Bo}} \left[-\frac{\partial^2}{\partial z^2} + q^2 - \frac{\partial \ln \epsilon(z)}{\partial z} \frac{\partial}{\partial z} \right] \quad (43)$$

$$\hat{M}_{\mathbf{q}}(z) = \frac{1}{4\pi l_{Bo}} \left[-\frac{\partial^2}{\partial z^2} + q^2 \right] \quad (44)$$

so that L is the length of region under consideration, which will be extended to infinity at appropriate place. Now, using identity for an arbitrary function $\hat{f}(z)$,

$$M_{\mathbf{q}}(z) \hat{f}(z) = \frac{\sqrt{\epsilon(z)}}{4\pi l_{Bo}} \left[-\frac{\partial^2}{\partial z^2} + q^2 + \frac{1}{\sqrt{\epsilon(z)}} \frac{\partial^2 \sqrt{\epsilon(z)}}{\partial z^2} \right] \left(\sqrt{\epsilon(z)} \hat{f}(z) \right) \quad (45)$$

we can write Eq. 42 as

$$\frac{H_{elec}}{k_B T} = \frac{1}{2\Delta z} \sum_{\mathbf{q}} \int_0^L dz \ln \epsilon(z) - \sum_{\mathbf{q}} \ln \left[\frac{\int D[\bar{\psi}_{\mathbf{q}}(z)] \exp \left(-\frac{1}{2} \int_0^L dz \bar{\psi}_{\mathbf{q}}(z) \bar{M}_{\mathbf{q},1}(z) \bar{\psi}_{-\mathbf{q}}(z) \right)}{\int D[\bar{\psi}_{\mathbf{q}}(z)] \exp \left(-\frac{1}{2} \int_0^L dz \bar{\psi}_{\mathbf{q}}(z) \bar{M}_{\mathbf{q},0}(z) \bar{\psi}_{-\mathbf{q}}(z) \right)} \right] \quad (46)$$

where Δz is the grid spacing used to discretize the space, $\bar{\psi}_{\mathbf{q}}(z) = \sqrt{\epsilon(z)} \hat{\psi}_{\mathbf{q}}(z)$ and

$$\bar{M}_{\mathbf{q},1}(z) = \left[-\frac{\partial^2}{\partial z^2} + \bar{q}^2(z) \right] \quad (47)$$

$$\bar{M}_{\mathbf{q},0}(z) = \left[-\frac{\partial^2}{\partial z^2} + q^2 \right] \quad (48)$$

so that $\bar{q}^2(z) = q^2 + \frac{1}{\sqrt{\epsilon(z)}} \frac{\partial^2 \sqrt{\epsilon(z)}}{\partial z^2}$. Now, evaluation of the second term on the right hand side of Eq. 46 can be done using methods for computation of functional determinants[54].

In particular, we use the notation

$$\frac{H_{elec}}{k_B T} = \frac{1}{2\Delta z} \sum_{\mathbf{q}} \int_0^L dz \ln \epsilon(z) + \frac{1}{2} \sum_{\mathbf{q}} \ln \left[\frac{Det [\bar{M}_{\mathbf{q},1}]}{Det [\bar{M}_{\mathbf{q},0}]} \right] \quad (49)$$

and $Det [\bar{M}_{\mathbf{q},1}]$ is given by the relation

$$Det [\bar{M}_{\mathbf{q},1}] = G_{\mathbf{q},1}(z = L) \quad (50)$$

where function $G_{\mathbf{q},1}$ satisfies

$$\bar{M}_{\mathbf{q},1}(z)G_{\mathbf{q},1}(z) = 0 \quad (51)$$

with the boundary conditions $G_{\mathbf{q},1}(0) = 0$ and $\left\{ \frac{\partial G_{\mathbf{q},1}(z)}{\partial z} \right\}_{|z=0} = 1$. Noting that $\bar{M}_{\mathbf{q},0}$ is a special case of $\bar{M}_{\mathbf{q},1}$ and corresponds to spatially invariant dielectric function, the same method can be used to compute $Det [\bar{M}_{\mathbf{q},0}]$. So far, we have mapped the problem of computing infinite eigenvalues for an operator on to a much simpler boundary value problem.

A general solution of Eq. 51 needs to be computed numerically. However, in the following, we use Wentzel-Kramers-Brillouin (WKB) approximation[55] to get insights into the effects of dielectric inhomogenities on the free energy of polymer blends. Introducing a length scale R (of the order of radius of gyration of polymers) to define dimensionless variables $\bar{z} = z/R, \bar{L} = L/R, \tilde{q} = qR$, WKB approximation gives an analytical expression for the solution of Eq. 51 in the limit of $R \rightarrow \infty$. Using the solution, Eq. 49 can be written as

$$\frac{H_{elec}}{k_B T} = \frac{1}{2\Delta z} \sum_{\mathbf{q}} \int_0^L dz \ln \epsilon(z) + \frac{1}{2} \sum_{\mathbf{q}} \ln \left[\frac{\sinh \left\{ \int_0^{\bar{L}} d\bar{z} \sqrt{\hat{q}^2(\bar{z})} \right\}}{\sinh \{ \tilde{q} \bar{L} \}} \frac{\tilde{q}}{\sqrt{\hat{q}(0)\hat{q}(\bar{L})}} \right] \quad (52)$$

where $\hat{q}^2(\bar{z}) = \tilde{q}^2 + \frac{1}{\sqrt{\epsilon(\bar{z})}} \frac{\partial^2 \sqrt{\epsilon(\bar{z})}}{\partial \bar{z}^2}$. For a planar interface between co-existing phase, $z = 0$ and $z = L$ corresponds to isotropic phases so that $\hat{q}(0) = \hat{q}(\bar{L}) = \tilde{q}$. In the limit of $L \rightarrow \infty, R \rightarrow \infty, \sum_{\mathbf{q}} = A \int d^2 q / (2\pi)^2$ and expanding the second term in powers of gradients of dielectric function, we get

$$\frac{H_{elec}}{k_B T} = \frac{A q_{max}^2}{8\pi \Delta z} \int_0^L dz \ln \epsilon(z) + \frac{A q_{max}}{8\pi} \int_0^L dz \frac{1}{\sqrt{\epsilon(z)}} \frac{\partial^2 \sqrt{\epsilon(z)}}{\partial z^2} \quad (53)$$

where q_{max} is the maximum value of wave-vector, introduced in order to regularize divergent integrals, whose origin lies in the divergent dipolar potential for $|\mathbf{r} - \mathbf{r}'| \rightarrow 0$.

For a homogeneous phase, the second term on the right hand side of Eq. 53 vanishes. In the next section, we show the effects of the leading term in Eq. 53 on the phase coexistence curves. However, the second term takes into account non-local effects relevant

for an inhomogeneous medium. Using integration by parts for the non-local term, we get

$$\frac{H_{elec}}{k_B T} = \frac{A q_{max}^2}{8\pi \Delta z} \int_0^L dz \ln \epsilon(z) + \frac{A q_{max}}{32\pi} \int_0^L dz \left[\frac{\partial \ln \epsilon(z)}{\partial z} \right]^2 \quad (54)$$

Such a functional form for the non-local effects of dielectric function allows us to study interfacial tension for a planar interface in the strong segregation limit as described below. Also, note that the functional form for the non-local effects of the dielectric function is similar to the one derived in Ref. [56] by transfer matrix approach.

III. RESULTS

A. Phase co-existence

It is well-known[47] that the homogeneous phase is one of the solutions of the saddle-point equations, which can be derived by optimizing the Hamiltonian given by Eqs. 36, 37 and 53 with respect to w_A, w_B and ρ_A . Carrying out the optimizations, we obtain

$$\phi_A(\mathbf{r}) = \frac{\rho_A^*(\mathbf{r})}{\rho_0} = i \left[\frac{n_A}{\rho_0} \frac{\delta \ln \bar{Q}_A}{\delta w_A(\mathbf{r})} \right]_{w_A=w_A^*} \quad (55)$$

$$1 - \phi_A(\mathbf{r}) = i \left[\frac{n_B}{\rho_0} \frac{\delta \ln \bar{Q}_B}{\delta w_B(\mathbf{r})} \right]_{w_B=w_B^*} \quad (56)$$

$$i w_A^*(\mathbf{r}) - i w_B^*(\mathbf{r}) = \chi_{AB} [1 - 2\phi_A(\mathbf{r})] + \frac{q_{max}^2 \Delta \epsilon}{8\pi \rho_0 \Delta z (1 + \Delta \epsilon \phi_A(z))} - \frac{q_{max} \Delta \epsilon}{16\pi \rho_0 [1 + \Delta \epsilon \phi_A(z)]} \frac{\partial^2 \ln [1 + \Delta \epsilon \phi_A(z)]}{\partial z^2} \quad (57)$$

where we have defined $\Delta \epsilon = (\epsilon_A - \epsilon_B)/\epsilon_B$. It can be checked explicitly that $\phi_A(\mathbf{r}) = \phi_A, w_A^* = \text{constant}$ and $w_B^* = \text{constant}$ satisfy these saddle-point equations. Furthermore, these parameters represent a homogeneous phase. The free energy of the homogeneous phase can be obtained by plugging this trivial solution of the saddle-point equations into the Eq. 29. Explicitly, we obtain the free energy of the homogeneous phase as

$$\begin{aligned} \frac{F_H}{\rho_0 V k_B T} = & \frac{\rho_0}{2} [w_{AA} \phi_A + w_{BB} (1 - \phi_A)] + \chi_{AB} \phi_A (1 - \phi_A) + \frac{\phi_A}{N_A} \left[\ln \left(\frac{\phi_A}{N_A} \right) - 1 \right] \\ & + \frac{1 - \phi_A}{N_B} \left[\ln \left(\frac{1 - \phi_A}{N_B} \right) - 1 \right] - \ln 4\pi + \frac{q_{max}^2}{8\pi \Delta z \rho_0} \ln [\epsilon_B + (\epsilon_A - \epsilon_B) \phi_A] \end{aligned} \quad (58)$$

where the subscript H stands for homogeneous. Here, the first term is the self-energy of the monomers taking into account the neutral interactions, the second term is the well-known

Flory-Huggins interaction energy and the next two terms represent the translational entropy of the chains. The fifth term is a constant obtained from the integration over the orientation of dipoles. The last term originates from the dipolar interactions.

If the dielectric constant of the blend is small i.e., $\epsilon_B + (\epsilon_A - \epsilon_B)\phi_A \ll 1$, we can expand the last term in Eq. 58 in powers of ϕ_A and second degree terms in ϕ_A appearing in Eq. 58 have the same functional forms as in Eq. 12. The condition of $\epsilon_B + (\epsilon_A - \epsilon_B)\phi_A \ll 1$ is met at high temperature or for monomers with very small dipole moments. This comparison reveals that analysis based on freely rotating dipoles has a very narrow parameter space where it is valid. Furthermore, the comparison reveals that $q_{max}^2/\Delta z = 1/\lambda^3$ in order for the two expressions to be the same.

The *exchange* chemical potential can be computed using the free energy given by Eq. 58. It is given by

$$\mu = \frac{\partial}{\partial \phi_A} \left[\frac{F_H}{\rho_o V k_B T} \right] = \frac{1}{2} [w_{AA} - w_{BB}] \rho_o + \chi_{AB}(1 - 2\phi_A) + \frac{1}{N_A} \ln(\phi_A) - \frac{1}{N_B} \ln(1 - \phi_A) + \frac{q_{max}^2 \Delta \epsilon}{8\pi \Delta z \rho_o (1 + \Delta \epsilon \phi_A)} \quad (59)$$

Spinodal can also be computed and is given by

$$\frac{\partial^2}{\partial \phi_A^2} \left[\frac{F_H}{\rho_o V k_B T} \right] = \frac{1}{N_A \phi_A} + \frac{1}{N_B (1 - \phi_A)} - 2\chi_{AB} - \frac{q_{max}^2 \Delta \epsilon^2}{8\pi \Delta z \rho_o (1 + \Delta \epsilon \phi_A)^2} = 0 \quad (60)$$

It is clear from these equations that it is the parameter $\Delta \epsilon = \epsilon_A/\epsilon_B - 1$, which captures the effect of dipolar interactions on phase equilibria. Also, note that the same parameter appears in the free energy of mixing (ΔF_{mix}) identified from Eq. 58 by writing it in the form

$$\begin{aligned} \frac{F_H}{\rho_o V k_B T} = & \phi_A \left[\frac{w_{AA} \rho_o}{2} - \frac{1}{N_A} - \ln 4\pi + \frac{q_{max}^2}{8\pi \Delta z \rho_o} \ln \epsilon_A \right] \\ & + (1 - \phi_A) \left[\frac{w_{BB} \rho_o}{2} - \frac{1}{N_B} - \ln 4\pi + \frac{q_{max}^2}{8\pi \Delta z \rho_o} \ln \epsilon_B \right] + \frac{\Delta F_{mix}}{k_B T} \end{aligned} \quad (61)$$

where

$$\begin{aligned} \frac{\Delta F_{mix}}{k_B T} = & \chi_{AB} \phi_A (1 - \phi_A) + \frac{\phi_A}{N_A} \ln \left(\frac{\phi_A}{N_A} \right) + \frac{1 - \phi_A}{N_B} \ln \left(\frac{1 - \phi_A}{N_B} \right) \\ & + \frac{q_{max}^2}{8\pi \Delta z \rho_o} \{ \ln [1 + \Delta \epsilon \phi_A] - \phi_A \ln [1 + \Delta \epsilon] \} \end{aligned} \quad (62)$$

Coexistence curves along with the spinodals are computed using above equations and presented in Figures 1 and 2. For the computations, we have taken $q_{max} = 2\pi/b$ and

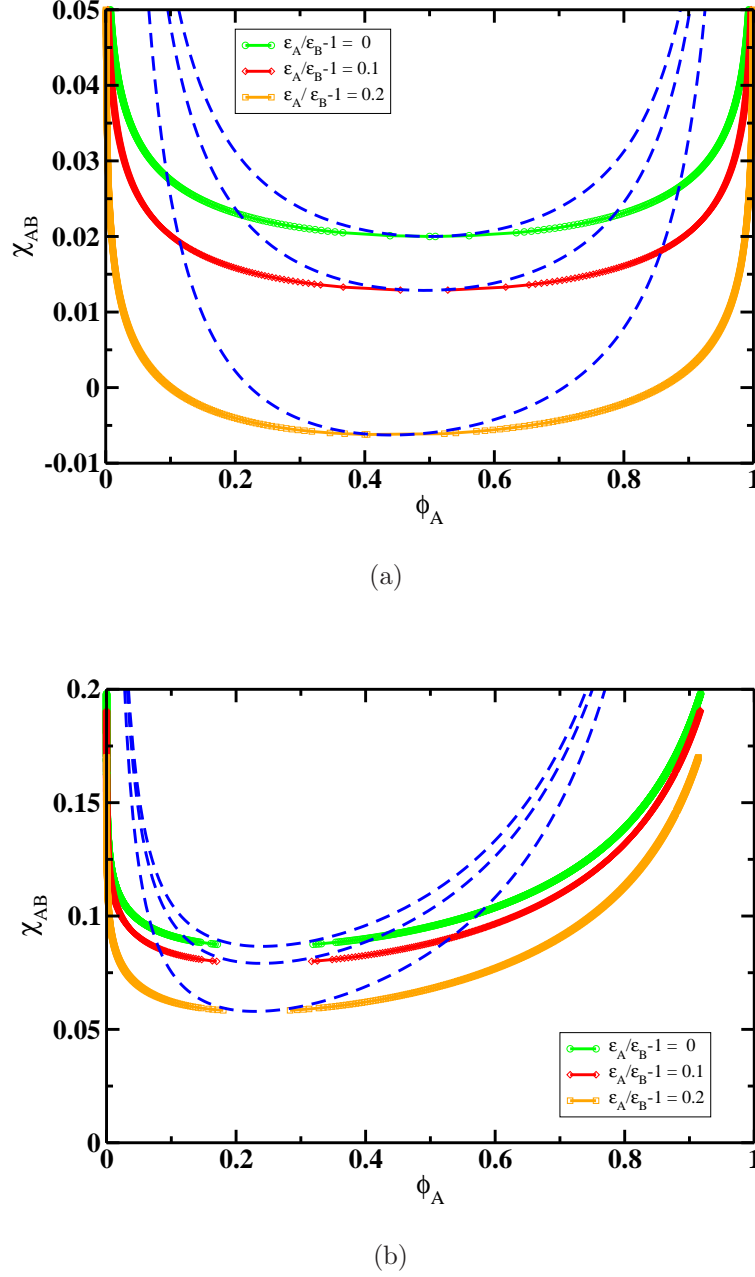


FIG. 1: Coexistence curves along with spinodals for symmetric ($N_A = N_B = 100$) and asymmetric chain lengths ($N_A = 100, N_B = 10$). The case of $\epsilon_A/\epsilon_B = 1$ corresponds to the Flory-Huggins theory.

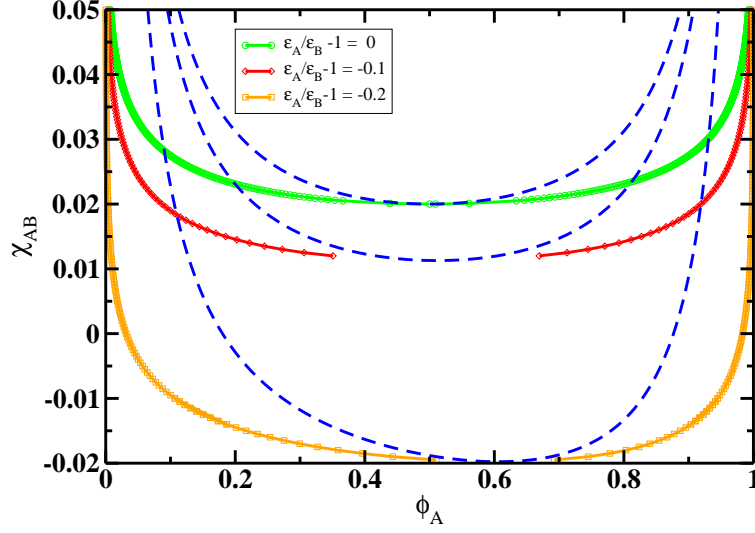
$\Delta z = b = \rho_o^{1/3}$. In these Figures, case of $\epsilon_A/\epsilon_B = 1$ corresponds to the Flory-Huggins theory as evident from the free energy of mixing (cf. Eq. 62). From the phase diagrams computed for symmetric and asymmetric chain lengths in Fig. 1, it is clear that differences in dielectric constants between the two polymers tend to induce phase segregation and

regime where uniformly mixed homogeneous phase is stable, shrinks with an increase in the dielectric mismatch. Note that the limiting case where the degree of polymerization of one of the polymers is unity corresponds to polymer solutions. Keeping this in mind, the theory presented here can be used to infer solubility of a polymer in different solvents[57]. It is clear from the results that polymers with dielectric constants similar to solvent have the largest uniformly mixed phase region. This is in agreement with the empirical rule of “like dissolves like”. Furthermore, comparison between Figures 1 and 2 reveals that the sign of the dielectric mismatch also plays a role in shifting the phase boundaries. Effects of the sign of the dielectric mismatch is clearer if one looks at the volume fraction and χ_{AB} at the critical point as shown in Fig. 3 for symmetric chain lengths $N_A = N_B = 100$. The critical point corresponds to minimum in the spinodal curve. From Fig. 3(a), it is found that the volume fraction of component A at the critical point decreases monotonically with an increase in $\Delta\epsilon$. Also, the χ_{AB} at the critical point increases and then decreases with an increase in $\Delta\epsilon$, with the maximum corresponding to $\Delta\epsilon = 0$ (cf. Fig. 3(b)). These shifts in the critical point originate from the dependence of the exchange chemical potential (cf. Eq. 59) on $\Delta\epsilon$ and ϕ_A . The maximum in Fig. 3(b) highlights the fact that the dielectric mismatch leads to enhanced phase segregation even with negative χ_{AB} . Similar shifts are found for systems with asymmetric chain lengths.

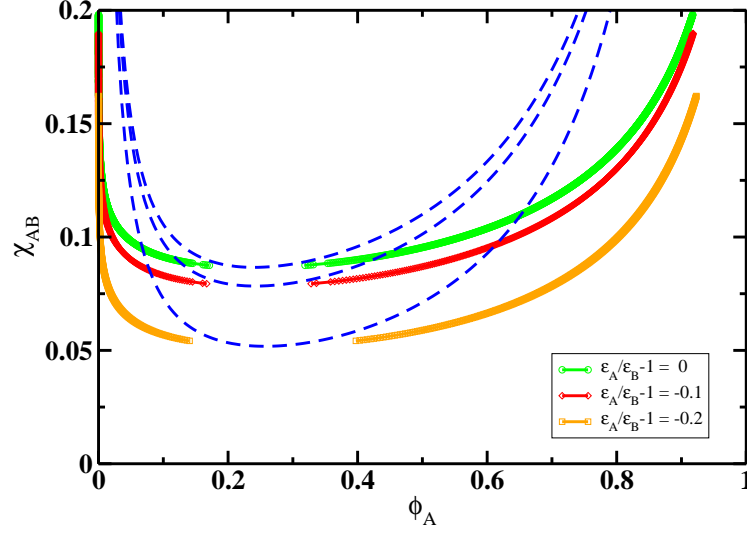
Note that the prediction of an enhanced phase segregation with an increase in the dielectric mismatch is in agreement with the treatment of freely rotating dipoles. However, note that the critical point also gets shifted (cf. Fig. 3) due to the mismatch, in contrast to being fixed for freely rotating dipoles. Due to the fact that the field theoretical formalism has the freely rotating dipoles as a limiting case, such a comparison highlights the invalidity of the assumption that dipoles can rotate freely in the two phase region. In the following, we use the field theoretical formalism to compute interfacial properties of a planar interface between the co-existing phases in the strong segregation limit.

B. Planar interface between the co-existing phases in the weak-coupling limit

A planar interface between the coexisting phases can be studied using formalism developed by Helfand-Tagami-Sapse[32–35] for very long polymers ($N_A = N_B \rightarrow \infty$). Using the formalism, we have studied interfacial tension and density profiles in the strong segregation



(a)

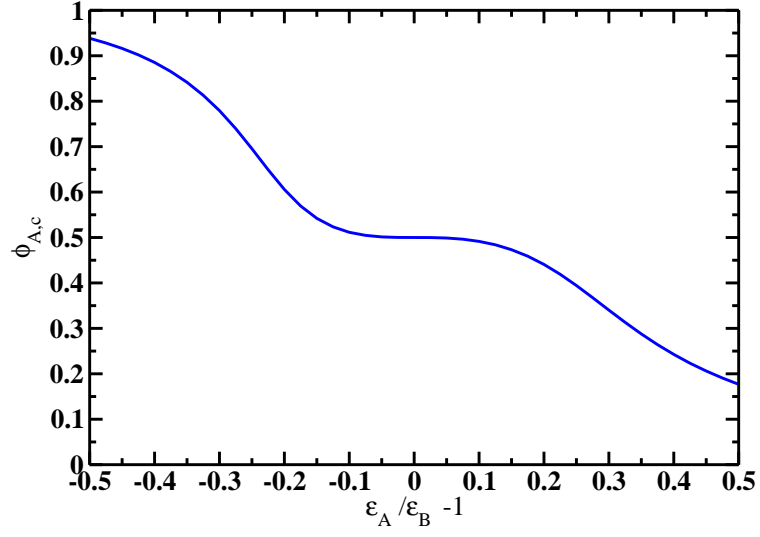


(b)

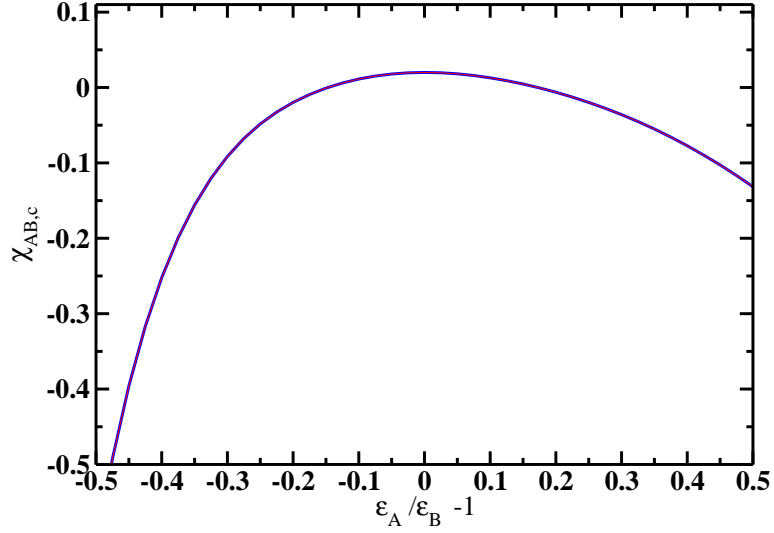
FIG. 2: Dependence of phase diagram on the sign of the dielectric mismatch is shown here by computing coexistence curves along with spinodals for symmetric ($N_A = N_B = 100$) and asymmetric chain lengths ($N_A = 100, N_B = 10$).

limit so that far from the interface, there are pure phases with corresponding volume fraction of a component approaching unity. In this limit, interfacial tension is independent of the value of N_A and N_B .

A straightforward mapping on to the formalism reveals that density profile of component



(a)



(b)

FIG. 3: Shifting of the critical point due to the dielectric mismatch is shown for systems with symmetric chain lengths ($N_A = N_B = 100$). The critical point is characterized by volume fraction $\phi_{A,c}$ and $\chi_{AB} = \chi_{AB,c}$ at the minimum of the spinodal curve, shown in (a) and (b), respectively.

A is given by

$$z = \frac{1}{2} \int_{1/2}^{\phi_A(z)} d\phi \left\{ \frac{\beta_A^2}{\phi} + \frac{\beta_B^2}{1-\phi} + \frac{q_{max} \Delta \epsilon^2}{8\pi [1 + \Delta \epsilon \phi]^2} \right\}^{1/2} \left\{ \frac{\Delta f^* \{\phi\}}{k_B T} \right\}^{-1/2} \quad (63)$$

with the zero of z taken so that $\phi_A(0) = 1/2$ and $\beta_k^2 = \rho_o b_k^2/6$ for $k = A, B$ is conformational

asymmetry parameter[35]. Also, Δf^* is the integrand for the free energy density of mixing in an inhomogeneous medium for $N_A \rightarrow \infty, N_B \rightarrow \infty$, given by

$$\frac{\Delta f^* \{\phi_A\}}{\rho_o k_B T} = \chi_{AB} \phi_A(z)(1 - \phi_A(z)) + \frac{q_{max}^2}{8\pi \Delta z \rho_o} \{ \ln [1 + \Delta \epsilon \phi_A(z)] - \phi_A(z) \ln [1 + \Delta \epsilon] \} \quad (64)$$

Interfacial tension for the interface between coexisting phases is given by

$$\frac{\gamma}{k_B T} = \int_0^1 d\phi \left\{ \frac{\beta_A^2}{\phi} + \frac{\beta_B^2}{1-\phi} + \frac{q_{max} \Delta \epsilon^2}{8\pi [1 + \Delta \epsilon \phi]^2} \right\}^{1/2} \left\{ \frac{\Delta f^* \{\phi\}}{k_B T} \right\}^{1/2} \quad (65)$$

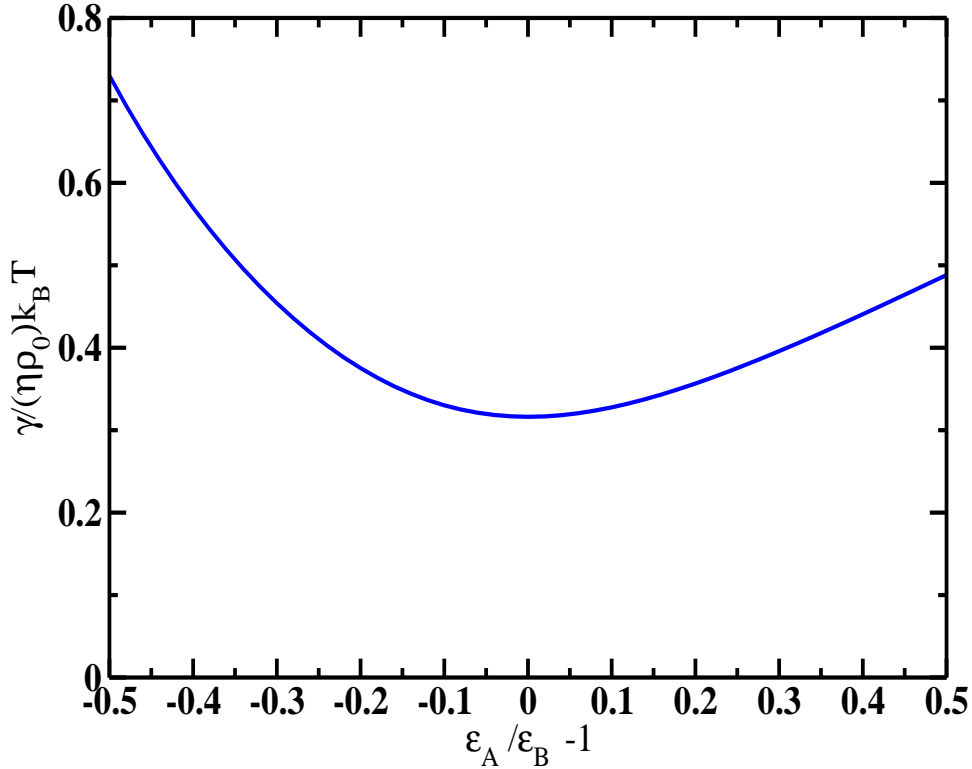


FIG. 4: Dependence of the interfacial tension on the dielectric mismatch for the conformationally symmetric polymer blends is shown here. $\chi_{AB} = 0.1$ is used in these calculations.

In order to highlight the effects of dielectric mismatch on interfacial properties, we consider a conformationally symmetric (i.e., $\beta_A = \beta_B = \beta$) polymer blend in this work. For the blend, we have computed density profiles and interfacial tension in units of parameter $\eta = \beta/\sqrt{\rho_o}$. Results for the interfacial tension are presented in Fig. 4. It is clear that the interfacial tension increases with an increase in the dielectric mismatch. However, amount of an increase in the interfacial tension depends on the sign of the dielectric mismatch parameter ($\Delta \epsilon$) due to asymmetric nature of the curve in Fig. 4 about $\Delta \epsilon = 0$. The asymmetric

nature arises due to the asymmetry of function Δf^* about $\Delta\epsilon = 0$. The increase in the interfacial tension with an increase in the mismatch parameter is a direct outcome of an increase in Δf^* , which also leads to sharper interfacial density profiles as shown in Fig. 5.

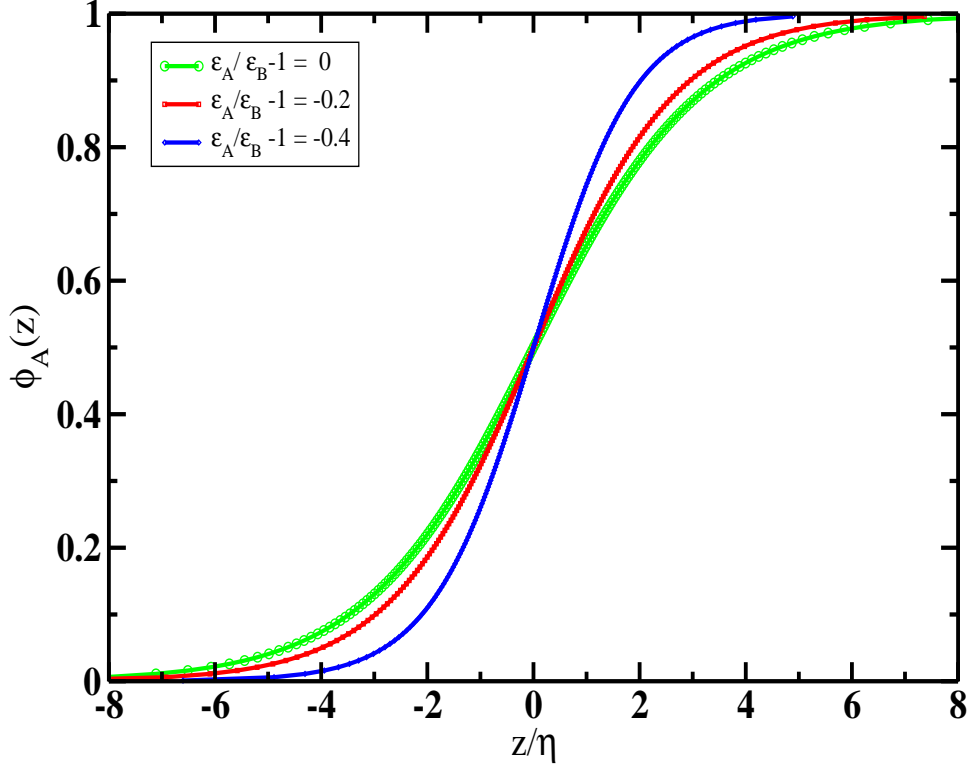


FIG. 5: Dependence of the volume fraction profiles on the dielectric mismatch is highlighted here. It is shown that an increase in the mismatch leads to sharper polymeric interfaces. $\chi_{AB} = 0.1$ is used in these calculations.

As the dielectric mismatch originates from a difference in dipole moments, it is clear that dipolar interactions induce phase segregation that subsequently causes sharper polymeric interfaces. The latter effect of an increase in sharpness of interfacial density profiles with an increase in the mismatch is in disagreement with the Cahn-Hilliard like treatment of freely rotating dipoles near the critical point, as presented in this paper. This comparison reveals another drawback of the treatment based on freely rotating dipoles for an inhomogeneous medium. Near the critical point, in addition to the assumption of freely-rotating dipoles in the two phase region, one needs to go beyond the saddle-point approximation invoked in the computation of the interfacial tension. For example, it is well-known[58] that one

needs to take into account fluctuations of the order parameter profiles in order to get the experimentally known exponents.

IV. CONCLUSIONS

A new method is developed to compute electrostatic contribution to the free energy. The method maps the evaluation of functional integrals over electrostatic collective variables on to the calculations of ratio of functional determinants frequently encountered in quantum mechanical systems[54]. Furthermore, the ratio of functional determinants is computed by mapping it on to the solution of a boundary value problem instead of computing infinite eigen values of different operators. The method allows the computation of free energy for a *given* dielectric function profile and can be readily applied to a number of problems where such a profile is known.

We have applied this method to study the effects of dipolar interactions in polymer blends. Parameters $l_{Bo}p_A^2$, $l_{Bo}p_B^2$ and $l_{Bo}p_Ap_B$ control the strengths of correlations due to dipolar interactions (as evident from Eq. 5) and local ordering of dipoles is expected[25] to compete with the macrophase separation in the low temperature regime. In this work, we have studied the high-temperature regime, where correlations due to orientation dependent dipolar interactions are negligible (weak coupling limit). In the weak coupling limit for the dipoles, the linear mixing rule based on the volume fractions serves as a good approximation for the local dielectric function. Using the linear mixing rule and newly developed method for the computation of electrostatic contributions, we have constructed a free energy expression for homogeneous phase and studied phase coexistence. Furthermore, a planar interface between the coexisting phases is studied by generalizing Helfand-Tagami-Sapse's formalism to dipolar polymer blends. It is found that dipolar interaction induces phase segregation. Furthermore, an increase in mismatch in monomeric dipole moments in polymer blends leads to an increase in interfacial tension with sharper interfaces between the co-existing phases. Magnitude of the effects of dipolar mismatch depends on the choice of cutoff (in the form of q_{max} in this work) below which short range interactions dominate over the dipole-dipole interactions. Detailed comparison with experiments in future can reveal sensitivity of the coexistence curves to the choice of cutoff.

Comparison of these theoretical predictions with those obtained from the treatment of

freely rotating dipoles reveals that the latter is valid in the *homogeneous* regime, where $\epsilon_A, \epsilon_B \sim 1$ (which corresponds to high temperature and weak dipole moments of monomers). Theoretical treatment based on the assumption of freely rotating dipoles in an inhomogeneous medium leads to erroneous predictions such as the insensitivity of critical point to the mismatch in monomeric dipole moments and a decrease in sharpness of interface between co-existing phases with an increase in the mismatch. Therefore, predictions from the field theory should be used for studies involving phase co-existence and a planar interface between the co-existing phases.

It is to be noted that the non-local contribution to the free energy in Eq. 54 is of the same functional form as in Ref. [56]. In Ref. [56], it was shown that the non-local term can be derived by considering non-retarded limit in a generalization of Lifshitz's theory[1] of van der Waals interactions, originally derived for discrete dielectric slabs, to study systems with continuous variation in the dielectric function. However, local incompressibility constraint used in this work differs from the classical theory of van der Waals. Also, we have ignored the effects of finite polarizability or the "induced" dipole moments, which has been shown to enhance the net dipole moments[2]. Neglecting the induction effect is a reasonable first step before the development of a comprehensive theory of the dielectric response of flexible macromolecules. In future, we plan to overcome this limitation of the theory using the field theoretical method developed here.

ACKNOWLEDGMENTS

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APPENDIX A : Field theory for dipolar polymer blends

A field theory for the polymer blends can be constructed following a standard protocol[47]. We start from the electrostatics contributions to the partition function. For the electrostatics contribution to the partition function written in the form Eq. 28, we use Hubbard-Stratonovich transformation in the form

$$\exp[-H_{dd}] = \frac{1}{\mu_\psi} \int D[\psi] \exp \left[i \int d\mathbf{r} \left\{ \nabla_{\mathbf{r}} \cdot \hat{P}_{ave}(\mathbf{r}) \right\} \psi(\mathbf{r}) + \frac{1}{8\pi l_{Bo}} \int d\mathbf{r} \psi(\mathbf{r}) \nabla_{\mathbf{r}}^2 \psi(\mathbf{r}) \right] \quad (\text{A-1})$$

where

$$\mu_\psi = \int D[\psi] \exp \left[\frac{1}{8\pi l_{Bo}} \int d\mathbf{r} \psi(\mathbf{r}) \nabla_{\mathbf{r}}^2 \psi(\mathbf{r}) \right] \quad (\text{A-2})$$

Using this transformation, we can evaluate the integrals over the orientations of the dipoles exactly. In particular, using

$$\begin{aligned} & \int \prod_{j=A,B} \prod_{\alpha=1}^{n_j} \prod_{s_{j,\alpha}=0}^{N_j} d\mathbf{u}_{j,\alpha}(s_{j,\alpha}) \exp \left[i \int d\mathbf{r} \left\{ \nabla_{\mathbf{r}} \cdot \hat{P}_{ave}(\mathbf{r}) \right\} \psi(\mathbf{r}) \right] \\ &= \int \prod_{j=A,B} \prod_{\alpha=1}^{n_j} \prod_{s_{j,\alpha}=0}^{N_j} \{ d\mathbf{u}_{j,\alpha}(s_{j,\alpha}) \exp [-ip_j \mathbf{u}_{j,\alpha}(s_{j,\alpha}) \cdot \nabla_{\mathbf{r}} \psi(\mathbf{r})] \} \\ &= \exp \left[\int d\mathbf{r} \sum_{j=A,B} \hat{\rho}_j(\mathbf{r}) \ln \left[\frac{4\pi \sin(p_j |\nabla_{\mathbf{r}} \psi(\mathbf{r})|)}{p_j |\nabla_{\mathbf{r}} \psi(\mathbf{r})|} \right] \right], \end{aligned} \quad (\text{A-3})$$

the partition function given by Eq. 1 becomes

$$\begin{aligned} Z &= \frac{1}{n_A! n_B!} \int \prod_{j=A,B} \prod_{\alpha=1}^{n_j} D[\mathbf{R}_{j,\alpha}] \frac{1}{\mu_\psi} \int D[\psi] \exp [-H_0 \{\mathbf{R}_{j,\alpha}\} - H_w \{\mathbf{R}_{j,\alpha}, \mathbf{R}_{j',\alpha'}\} \\ &+ \frac{1}{8\pi l_{Bo}} \int d\mathbf{r} \psi(\mathbf{r}) \nabla_{\mathbf{r}}^2 \psi(\mathbf{r}) + \int d\mathbf{r} \hat{\rho}_A(\mathbf{r}) \ln \left[\frac{4\pi \sin(p_A |\nabla_{\mathbf{r}} \psi(\mathbf{r})|)}{p_A |\nabla_{\mathbf{r}} \psi(\mathbf{r})|} \right] \\ &+ \int d\mathbf{r} \hat{\rho}_B(\mathbf{r}) \ln \left[\frac{4\pi \sin(p_B |\nabla_{\mathbf{r}} \psi(\mathbf{r})|)}{p_B |\nabla_{\mathbf{r}} \psi(\mathbf{r})|} \right]] \prod_{\mathbf{r}} \delta[\hat{\rho}_A(\mathbf{r}) + \hat{\rho}_B(\mathbf{r}) - \rho_0] \end{aligned} \quad (\text{A-4})$$

Rewriting H_w given by Eq. 3 using the local incompressibility constraint as

$$H_w \{\mathbf{R}_{j,\alpha}, \mathbf{R}_{j',\alpha'}\} = \frac{1}{2} [w_{AA} n_A N_A + w_{BB} n_B N_B] \rho_0 + \chi_{AB} b^3 \int d\mathbf{r} \hat{\rho}_A(\mathbf{r}) \hat{\rho}_B(\mathbf{r}) \quad (\text{A-5})$$

where we have defined a dimensionless chi parameter by

$$\chi_{AB} b^3 = w_{AB} - \frac{w_{AA} + w_{BB}}{2} \quad (\text{A-6})$$

Now, we introduce collective variables corresponding to $\hat{\rho}_j$ by using the identity

$$Z \{ \hat{\rho}_A, \hat{\rho}_B \} = \int D[\rho_A] \int D[\rho_B] Z \{ \rho_A, \rho_B \} \prod_{\mathbf{r}} \delta [\rho_A(\mathbf{r}) - \hat{\rho}_A(\mathbf{r})] \prod_{\mathbf{r}} \delta [\rho_B(\mathbf{r}) - \hat{\rho}_B(\mathbf{r})]$$

and write the local constraints (represented by delta functions) in terms of functional integrals using

$$\prod_{\mathbf{r}} \delta [\rho_j(\mathbf{r}) - \hat{\rho}_j(\mathbf{r})] = \int D[w_j] \exp \left[i \int d\mathbf{r} w_j(\mathbf{r}) \{ \rho_j(\mathbf{r}) - \hat{\rho}_j(\mathbf{r}) \} \right] \quad (\text{A-7})$$

for $j = A, B$.

Using these transformations and evaluating a trivial functional intergral over ρ_B , we can write the partition function as

$$Z = \frac{1}{\mu_\psi} \int D[\rho_A] \int D[w_A] \int D[w_B] \int D[\psi] \exp \left[-\frac{F_0}{k_B T} - \frac{H}{k_B T} \right] \quad (\text{A-8})$$

where

$$\frac{F_0}{k_B T} = \frac{1}{2} [w_{AA} n_A N_A + w_{BB} n_B N_B] \rho_0 + \ln \left[\frac{n_A! n_B!}{(4\pi)^{\sum_{j=A,B} n_j N_j} \prod_{j=A,B} Q_j^{n_j} \{0\}} \right] \quad (\text{A-9})$$

and

$$\begin{aligned} \frac{H}{k_B T} = & \chi_{AB} b^3 \int d\mathbf{r} \rho_A(\mathbf{r}) (\rho_0 - \rho_A(\mathbf{r})) - i \int d\mathbf{r} w_A(\mathbf{r}) \rho_A(\mathbf{r}) - i \int d\mathbf{r} w_B(\mathbf{r}) [\rho_0 - \rho_A(\mathbf{r})] \\ & - \frac{1}{8\pi l_{Bo}} \int d\mathbf{r} \psi(\mathbf{r}) \nabla_{\mathbf{r}}^2 \psi(\mathbf{r}) - \int d\mathbf{r} \rho_A(\mathbf{r}) \ln \left[\frac{\sin(p_A |\nabla_{\mathbf{r}} \psi(\mathbf{r})|)}{p_A |\nabla_{\mathbf{r}} \psi(\mathbf{r})|} \right] \\ & - \int d\mathbf{r} \{ \rho_0 - \rho_A(\mathbf{r}) \} \ln \left[\frac{\sin(p_B |\nabla_{\mathbf{r}} \psi(\mathbf{r})|)}{p_B |\nabla_{\mathbf{r}} \psi(\mathbf{r})|} \right] - \sum_{j=A,B} n_j \ln \bar{Q}_j \{w_j\} \end{aligned} \quad (\text{A-10})$$

where $Q_j \{0\} = \int D[\mathbf{R}] \exp \left[-\frac{3}{2b_j^2} \int_0^{N_j} ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 \right] = V$, V being the total volume and

$$\bar{Q}_j \{w_j\} = \frac{Q_j \{w_j\}}{Q_j \{0\}} = \frac{\int D[\mathbf{R}] \exp \left[-\frac{3}{2b_j^2} \int_0^{N_j} ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 - i \int_0^{N_j} ds w_j(\mathbf{R}) \right]}{\int D[\mathbf{R}] \exp \left[-\frac{3}{2b_j^2} \int_0^{N_j} ds \left(\frac{\partial \mathbf{R}}{\partial s} \right)^2 \right]} \quad (\text{A-11})$$

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Enhanced phase segregation induced by dipolar interactions in polymer blends

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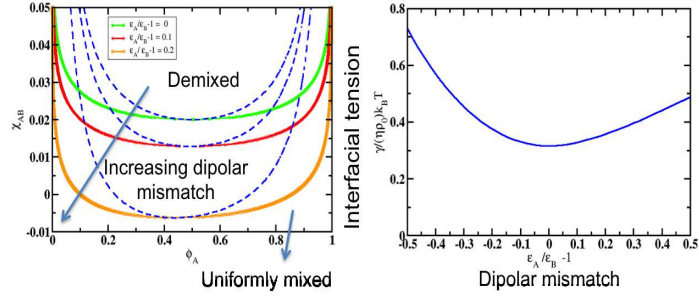


FIG. 6: Table of Contents Graphic

